De reactie van 1-alkynyl-ethers met carbonzuren; een studie van het mechanisme

Zwanenburg, Binne

SUMMARY

This thesis deals with the mechanism of the reaction between ethoxyethyne and carboxylic acids in non-aqueous solvents. Ethyl acetate and carboxylic acid anhydrides are the end products of this reaction, while 1-ethoxyvinyl esters are intermediates.

$$HC{\equiv}C{-}OC_2H_5 + RCOOH \longrightarrow H_2C{=}C(OC_2H_5)OCOR$$

$$H_2C{=}C(OC_2H_5)OCOR + RCOOH \longrightarrow H_3C{-}C(OC_2H_5)(OCOR)_2 \downarrow$$

$$H_3CCOOC_2H_5 + (RCO)_2O$$

After an introduction to the problem, in chapter 1, the syntheses of the different compounds and the methods of analysis are described in chapter 2. The concentration of 1-ethoxyvinyl esters and of 1-alkynyl ethers could be determined iodometrically. The concentration of ethoxyethyne was also determined argentometrically.

The second part of the reaction sequence, the reaction of 1-ethoxyvinyl esters with carboxylic acids is treated in chapter 3.

The kinetics in benzene follow the rate equation

$v = k_3 \cdot c_{1\text{-ethoxyvin yl ester}} \cdot c^2_{\text{acid}}$.

In dioxane and sulfolane the following equation is obeyed:

$v = (k^0_3 \cdot c^2_{\text{acid}} + k_4 \cdot c^3_{\text{acid}}) \cdot c_{1\text{-ethoxyvin yl ester}}$.

The rate constants in sulfolane are 20—30 times as large as the ones in dioxane, while the rate constants in benzene are approximately equal to the ones in sulfolane.

The kinetic isotope effect, k_H/k_D, for the reaction of O-deutero acetic acid compared to normal acetic acid with 1-ethoxyvinyl acetate, amounts to 4.0 in benzene and to 3.6 in sulfolane as solvent. During this reaction no deuterium was taken up in the vinyl ester molecule.

Addition of tetrabutylammonium perchlorate to the solvent diox-

ane increased the rate constant of the reaction between 1-ethoxyvinyl chloroacetate and chloroacetic acid. This rate constant could be expressed by the linear equation $k_3 = (k_3)_{\text{conc salt} = 0} \cdot (1 + b \cdot c_{\text{salt}})$ in which the value of b was 4 l/mole.

From these results it was concluded, that in a number of pre-equilibria a solvation complex is formed between an 1-ethoxyvinyl ester molecule and two, three or four molecules of carboxylic acid. These pre-equilibria are followed by the rate determining step in which a proton is transferred to the substrate giving an ion pair as intermediate. From this ion pair the diadduct $H_3C—C(OC_2H_5)(OCOR)_2$ is formed, which decomposes in a fast step to ethyl acetate and anhydride.

The first step of the reaction sequence, the reaction between ethoxyethyne and carboxylic acid, is treated in chapter 4.

By mathematical analyses of a system of two consecutive third order reactions, it was shown that the decrease of the alkyne concentration is not appreciably affected by the second reaction when the acid concentration is sufficiently high.

The rate expressions for ethoxyethyne and other 1-alkynyl ethers as substrates have the same forms as given above for the ethoxyvinyl esters.

A considerable rate enlargement was observed by varying the solvent from dioxane to sulfolane, while the rate in benzene is approximately equal to the one in sulfolane.

From measurements on the reaction of ethoxyethyne and either CH_3COOH or CH_3COOD in benzene a kinetic isotope effect, k_H/k_D, of 3.1 was observed. In sulfolane as solvent, k_H/k_D was equal to 2.8 for the third order and to 2.7 for the fourth order contribution.

From infrared spectra of reaction mixtures of ethoxyethyne and O-deutero acetic acid in the chosen solvents, it was concluded, that no exchange of deuterium had taken place during the reactions in the solvents benzene and sulfolane. In dioxane, however, deuterium was taken up in the ethoxyethyne.

The effect of added tetrabutylammonium perchlorate on the rate of the reaction of ethoxyethyne and chloroacetic acid in dioxane can be expressed by the equation

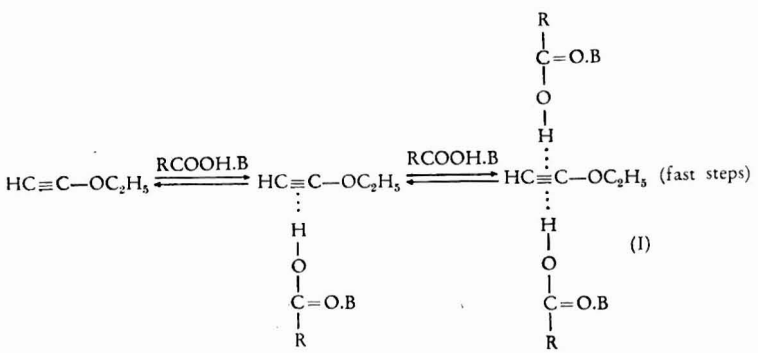
$$k_1/\bar{c}_A^2 = (k_1/\bar{c}_A^2)_{\text{conc salt} = 0} \cdot (1 + b \cdot c_{\text{salt}}).$$

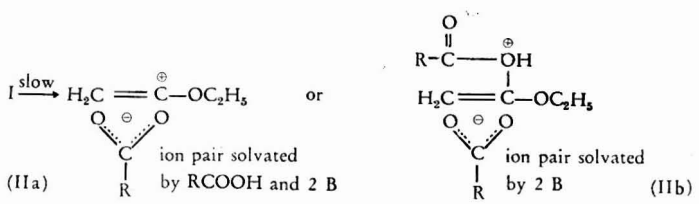
The coefficient b was equal to 8 l/mole.

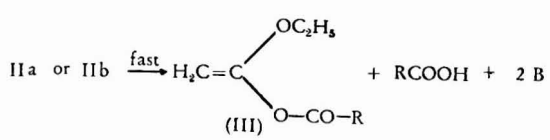
Variations in the structure of the 1-alkynyl ether molecule are analyzed with a TAFT equation. A linear free energy relationship of the form log k = $\varrho^*\sigma^*$ + constant is obeyed by the rate constants of the reaction of acetic acid and the compounds $R'C{\equiv}C{-}OC_2H_5$ with R′ CH_3, C_2H_5 and iso-C_3H_7 in benzene and sulfolane as solvents.

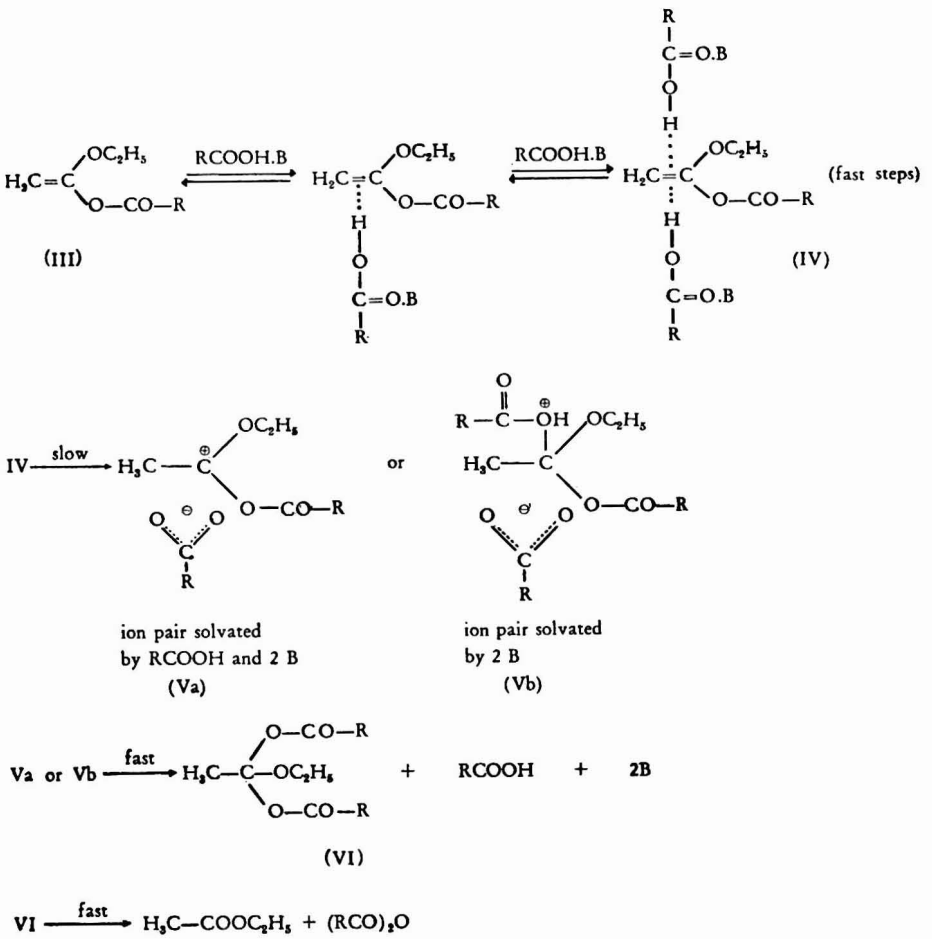
It was concluded, that the mechanism of the first part of the reaction sequence is analogous to the one for the second part.

The results of the experiments described in this thesis, are consistent with the following mechanism for the reaction of ethoxyethyne and a carboxylic acid in non-aqueous solvents.









In this scheme B represents in benzene a carboxylic acid molecule and in the other solvents an acid or a solvent molecule. The deuterium exchange in dioxane is in accordance with this scheme if ion pair return is taken into consideration.

The mechanism is probably generally valid for the reaction of 1-alkynyl ethers with carboxylic acids in non-aqueous solvents.